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<b>(21) International Application Number:</b> PCT/EP97/00202 <b>(22) International Filing Date:</b> 15 January 1997 (15.01.97)  <b>(30) Priority Data:</b> 9602797.4 12 February 1996 (12.02.96) GB  <b>(71) Applicant (for all designated States except US):</b> CROSFIELD LIMITED [GB/GB]; Bank Quay, Warrington, Cheshire WA5 1BA (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BAINES, Pamela [GB/GB]; 11 Withycombe Road, Penketh, Warrington, Cheshire WA5 2QL (GB). STANIER, Peter, William [GB/GB]; 66 Grange Way, Elworth, Sandbach, Cheshire CW11 9ES (GB).  <b>(74) Agent:</b> COLLINGWOOD, Anthony, Robert; ICI Group Intellectual Property, P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> INORGANIC MATERIAL IN PARTICLES FORM  <b>(57) Abstract</b>  A cosmetic composition includes an inorganic material in granular form which, under condition of use of the cosmetic composition, breaks down to a particle size wherein less than 5 % by weight, preferably less than 2 % by weight, most preferably less than 1 % by weight is above 45 microns, as measured by wet sieve analysis.		

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INORGANIC MATERIAL IN PARTICLES FORMField of the Invention

5 The present invention relates to an inorganic material in particles form useful in cosmetic compositions. The present invention most specifically relates to an exfoliating and/or massaging and/or cleansing material. The present invention also relates to a cosmetic composition containing said  
10 inorganic material.

Background of the Invention

15 Exfoliation and cleansing of the skin is an essential element of body care. Exfoliating compositions are well known in the art. Such compositions may, by abrasion, remove residual make-up and dead cells from the surface of the skin in order to prevent pores clogging. This is achieved by abrasive particles suspended in said compositions.

20 In the past, two particulate abrasive materials were used; calcium carbonate and the endocarp of apricot seeds. It was recently recognized that these abrasive materials had an inherent grittiness and that it was desirable to produce an  
25 abrasive material which has an initial skin feel which would disappear while using the cosmetic formulation.

30 Thus, it has been disclosed in EP-A-670,712 an exfoliating composition including a particulate exfoliating material with a particle size in the range of 0.03 to 3mm, wherein the particulate material comprises an agglomerated silica having a primary particle size in the range of 0.01-0.2 microns, which is friable and under conditions of use of the composition break up into particles having an average size of  
35 less than 40 microns.

Only one type of silica agglomerate is disclosed in this document and it is described as an agglomerate of Sident 22S.

5 It is disclosed in this document that the inherent grittiness of the suspended abrasive particles is avoided. It is further disclosed that particles with average size of less than 40 microns do not feel gritty and that the average particle size, after break up of the exfoliating particles, will be less than 40  $\mu\text{m}$ .

10 Nevertheless, it has been found that, whilst the grittiness is reduced, the particles are still felt by the user as a residue on the skin.

15 A desirable feature following particle breakdown would be the perception by the user of a creamy smooth lather of the product on the skin and gentle cleansing. It has been found that the use of silica agglomerates as described in EP-A-670,712 did not give this effect because they do not fully  
20 breakdown and therefore do not contribute, by way of a thickening effect that smaller particles can provide, to the resultant lather.

25 There is therefore a need for exfoliating particles which, whilst providing the required exfoliating performance, progressively break down to a point at which they are no longer detected. It is also desirable for such exfoliating particles to give a creamy, smooth lather on breakdown in a cosmetic composition.

30

Tests and Definitions

## i) Oil Absorption

5 The oil absorption is determined by the ASTM spatula rub-out method (American Society Of Test Material Standards D, 281).

10 The test is based on the principle of mixing linseed oil with the silica by rubbing with a spatula on a smooth surface until a stiff putty-like paste is formed which will not break or separate when it is cut with a spatula. The volume of oil used is then put into the following equation:-

15

$$\begin{aligned}\text{Oil absorption} &= \frac{\text{cm}^3 \text{ oil absorption} \times 100}{\text{Wt. of silica sample in g}} \\ &= \text{cm}^3 \text{ oil}/100 \text{ g silica}\end{aligned}$$

## ii) Weight Mean Particle Size

20

25 The weight mean particle size of the water insoluble particulate before agglomeration is determined using a Malvern Mastersizer model X, made by Malvern Instruments, Malvern, Worcestershire with MS15 sample presentation unit. This instrument uses the principle of Fraunhofer diffraction, utilising a low power He/Ne laser. The water insoluble particulates are dispersed ultrasonically in water for 7 minutes to form an aqueous suspension and then mechanically stirred before they are subjected to the measurement procedure outlined in the instruction manual for the instrument, utilising a 45 mm

30

35 lens in the detector system.

The Malvern Particle Sizer measures the weight particle size of the water insoluble particulate. The weight mean particle size ( $d_{50}$ ) or 50 percentile, the 10 percentile ( $d_{10}$ ) and the 90 percentile ( $d_{90}$ ) are easily obtained from the data generated by the instrument.

iii) Granular Strength

EP-A-670712 describes a test to measure agglomerate strength in dry powder conditions. It is considered that this test is not representative of the conditions which prevail when a cosmetic composition is used and the granules are breaking down in an aqueous system.

It was therefore necessary to develop a more representative test, which is carried out in the presence of water and subjects the granule to controlled de-aggregation.

Granule breakdown characterisation was carried out using a Microson XL2020 Sonicator programmable ultrasonic liquid processor, manufactured by Misonix Inc. Farmingdale, New York and supplied in the UK by Labcaire Systems Ltd, Avon.

The Microson XL2020 Sonicator ultrasonic processor has a maximum of 550 watts output with a 20KHz convertor and is fitted with a 3/4 inch tapped horn. The processor has variable amplitude control and a microprocessor controlled digital timer integrated with a Pulsar cycle timer with power output and elapsed time displays.

The piezoelectric convertor transforms electrical energy to mechanical energy at a frequency of 20KHz.

Oscillation of piezoelectric crystals is transmitted and

focused by a titanium disruptor horn that radiates energy into the liquid being treated. A phenomenon known as cavitation, the formation and collapse of microscopic vapour bubbles generated by the strong sound waves produces a shearing and tearing action. Almost all of the activity takes place just in front of the probe tip.

The generator provides high voltage pulses of energy at 20 KHz and adjusts for varying load conditions, such as viscosity and temperature. It senses impedance change and increases or decreases power to the probe tip automatically.

The 3/4 inch probe is a medium intensity horn for processing volumes between 25 and 500 ml. The maximum amplitude at the tip of the probe is 60 microns. Hence, sonicator processors operating at output control setting 10 have 60 microns of amplitude (peak to peak amplitude of the radiating face of the tip) at the tip of the probe.

Therefore, there is a linear relationship between the output control knob (or amplitude adjustment knob) and the amplitude at the tip of the probe., ie 6 micons of amplitude per control knob setting. The generator draws energy accordingly to maintain a constant amplitude at the tip for a given output control setting. This is displayed on the % output power meter and is energy in Watts (ie output =  $\% / 100 * 550$  watts available = x watts delivered)

A paper given by Mr S Berliner, (Director, Technical Services, Heat Systems-Ultrasonics Inc.) at the 9th Annual Technical Symposium of the Ultrasonic Industry

Association, entitled "Application of Ultrasonic Processors (Power vs Intensity in Sonification)" provides further detailed information of the principles involved in this experimental technique.

Procedure:

A 250 ml pyrex beaker is insulated and fitted with a lid with a 3/4 inch hole in the centre to accommodate the ultrasonic probe and a 1/8 inch hole to the side to accommodate a temperature probe.

Into the insulated beaker weigh the desired amount of deionised water, maintained at a constant temperature of 21°C and the desired amount of inorganic granule to obtain a final weight of 200 g. A magnetic stirrer bar is introduced into the beaker and the beaker is placed on a magnetic stirrer hotplate equipped with a temperature sensor (Heidolph MR3003 magnetic stirrer hotplate with a stainless steel PT-100 temperature sensor and rpm stirrer speed, obtainable from Orme Scientific, Manchester. The beaker contents are stirred on setting 3 (~300 rpm), the ultrasonic probe is immersed to a depth of 5/8 inch into the liquid and the temperature sensor is inserted into the liquid to continuously monitor temperature.

The Sonicator ultrasonic processor is switched on and information on processing time and pulsed mode programmed, as required.

Cavitation is introduced to the system by turning the output control knob to the desired amplitude setting, whilst the temperature profile is closely monitored. The % power output required to maintain the amplitude at

the tip is also recorded, according to the setting.

When the cavitation process is complete, the stirrer is switched off and the magnetic stirrer bar is removed. Manual stirring is continued with a spatula to maintain dispersion.

#### +45 micron Wet Sieve Test Method

The inorganic particle dispersion is poured through a 45 micron sieve. Any residue in the beaker is washed through the sieve, using half the amount of initial water. The sieve is then dried to constant weight in an oven at 105°C. The residue which remains on top of the 45 micron sieve is then weighed and expressed as a percentage of the initial weight of inorganic granule. The greater the amount retained on the sieve, the stronger the agglomerate strength of the granule and the more difficult it is to breakdown. An optimum product will have no residue remaining on the sieve.

It has been found that, for a granule to satisfactorily breakdown in cosmetic compositions, it will have less than 5%, preferably less than 2%, most preferably less than 1% by weight, residue on a +45 micron sieve after ultrasonification on setting 10 (60 micron amplitude) for a period of 7 minutes.

#### iv) Particle Size Distribution by Sieve Analysis

An accurate measure of the true particle size distribution of the granular composition is done using sieve analysis.

100 g of the sample is placed on the top sieve of a series of BS sieves, at approximately 50 micron intervals to cover the particle size range of the granule. The sieves are arranged in order with the finest at the bottom and the coarsest at the top of the stack. The sieves are placed in a mechanical vibrator eg Inclyno Mechanical Sieve Shaker by Pascall Engineering Co. Ltd., covered with a lid and shaken for 10 minutes. Each sieve fraction is accurately weighed and the results calculated:

$$\% \text{ residue} = \frac{\text{Wt. of residue} * 100}{\text{Wt. of sample}}$$

v) BET surface area

Surface area is determined using standard nitrogen adsorption methods of Brunauer, Emmett and Teller (BET), using a single point method with a Sorpty 1750 apparatus supplied by Carlo Erba company of Italy. The sample was outgassed under vacuum at 270°C for 1 hour before measurement.

General Description of the Invention

It is a first object of the present invention to provide an inorganic material in granular form having a granular strength such that less than 5%, preferably less than 2%, most preferably less than 1% by weight, residue remains on a 45 micron wet sieve after ultrasonification for 7 minutes with 60 micron amplitude of vibration.

Preferably, the inorganic material comprises at least 95% by weight of amorphous silicas.

More preferably, the inorganic material comprises at least 95% by weight of amorphous silica agglomerates.

5 Even more preferably the inorganic material in granular form comprises at least 95% w/w of a water insoluble particulate, whereby 5 to 90% of the water insoluble particulate is made from a water insoluble particulate material, having a weight mean particle size of less than 20 microns and an oil  
10 absorption capacity of 90 to 145 cm<sup>3</sup>/100g, and selected from the group consisting of amorphous silicas, aluminas, calcium carbonates, dicalcium phosphate, tribasic calcium phosphates, insoluble sodium metaphosphate, calcium pyrophosphates, hydroxyapatites, perlites, zeolites, magnesium carbonate, pumice, and 5 to 90% of the water insoluble particulate is  
15 made from an amorphous silica, having a weight mean particle size of below 20 microns and an oil absorption 150 to 190 cm<sup>3</sup>/100g.

20 Also more preferably the inorganic material in granular form comprises at least 95% w/w of a water insoluble particulate, whereby 5 to 90% of the water insoluble particulate is made from a water insoluble particulate material, having a weight mean particle size of less than 20 microns and an oil  
25 absorption capacity of 90 to 145 cm<sup>3</sup>/100g, and selected from the group consisting of aluminas, calcium carbonates, dicalcium phosphate, tribasic calcium phosphates, insoluble sodium metaphosphate, calcium pyrophosphates, hydroxyapatites, perlites, zeolites, magnesium carbonate, pumice, and 5 to 90% of the water insoluble particulate is  
30 made from an amorphous silica, having a weight mean particle size of below 20 microns and an oil absorption 130 to 190 cm<sup>3</sup>/100g.

35 Preferably, the inorganic material has a particle size of 95% below 1000 microns and 95% above 45 microns, as measured by

sieve analysis.

The inorganic material in granular form can be produced by any agglomeration or compaction technique.

Agglomeration can be achieved for example by pan granulation, dry roller compaction, extrusion, spray granulation or spinning disc granulation.

When the agglomeration is performed in a pan granulator, the water:solids ratio for products of this invention is preferably in the range 1.0:1 to 1.25:1. This ratio is important to achieve agglomerates of correct strength, since below this the material remains a powder and above this a paste is formed. Using this method the agglomerates need to be dried. This drying can be done in several ways, eg in an oven or in a fluidised bed. During this drying stage, the required degree of strength is built into the agglomerates.

Once compacted, the agglomerates are then reduced in size according to the desired particle size range in the product application.

Owing to the porous nature of the agglomerates, it is possible for them to act as delivery vehicles for substances that give cosmetic benefits such as colouring pigments, flavours, perfumes or other cosmetic ingredient. Such substances may be contained within the pores of the material.

If coloured granules are required, then suitable coloured pigments, for example pigment dispersions under the Cosmenyl trade name or pigment powders under the Hostaperm trade name or Cosmetic Pink RC 01 (D & C Red No 30) supplied by Hoechst or Ultramarine Grade 54 supplied by Holliday Pigments, can be added to the composition of the granule, without affecting

the strength of the granule.

It is a second object of the present invention to provide a cosmetic composition comprising such inorganic material in granular form.

When a cosmetic composition is used, for example by hand massage on the skin, the shear and crush forces which are created cause the particles of inorganic material in granular form to break up after a short period of time, typically from 10 to 25 seconds, preferably less than 20 seconds, to such an extent that they can no longer be felt.

It is a third object of the present invention to provide a cosmetic composition including an inorganic material in granular form, characterised in that the inorganic material in granular form, under condition of use of the cosmetic composition, breaks down to a particle size wherein less than 5% by weight, preferably less than 2% by weight, most preferably less than 1% by weight is above 45 microns, as measured by wet sieve analysis.

Preferably, the cosmetic composition is in the form of a liquid, an emulsion or a multiple emulsion. By suitable adjustment of the solid to liquid ratio, and the viscosity of the liquid phase, the composition may take any physical form from a thick paste or gel to a low viscosity liquid.

In the cosmetic compositions of the present invention, the level of inorganic material in granular form may be from 1 to 20% by weight, preferably 1 to 10%, more preferably 3 to 10% by weight, even more preferably 3 to 5%.

The cosmetic composition of the invention may contain one or more additional components depending on the end use of the

product, typical end uses being personal wash off products for example shower gels, facial cleansers and shampoos.

5 Cleaning compositions also comprise one or more surfactants, preferably selected from anionic, nonionic, amphoteric and zwitterionic surfactants and mixtures thereof. The surfactants may be present in a total amount of from 1% to 50% by weight, preferably from about 2% to 30% by weight.

10 Water is another component of the cosmetic compositions of the present invention and may be present in an amount from 10% to 90% by weight, preferably from 20% to 80% by weight, more preferably from 40% to 75% by weight.

15 In cosmetic compositions of the present invention it is preferred that one or more thickening or suspending agents are included in order that the inorganic material in granular form remains stably dispersed throughout the composition. These agents may be present in the compositions in a total  
20 amount of from 0.1 to 60% by weight depending on the nature of the agents.

The cosmetic compositions of the invention may also contain other components conventionally found in cosmetic  
25 compositions for hair or skin.

Compositions in accordance with the present invention may be made by conventional methods of preparing cosmetic compositions, eg facial scrubs. If suspension is through  
30 surfactant lamellar phase formation, however, it is preferable that the particulate material is incorporated in the composition prior to the formation of the lamellar phase which stabilises the dispersed particles, in order for the particulate material to be successfully and stably  
35 incorporated therein. Alternatively, for creams and pastes,

the base composition may be prepared by mixing the base ingredients, with addition of thickener or suspending agent if used, followed by low shear mixing of the pre-prepared particulate material.

5

It is important that in the preparation of compositions in accordance to the present invention and any mixing be done at sufficiently low shear that the inorganic material in granular form does not experience forces sufficiently great to cause the particles to fracture.

10

#### Detailed Description of the Invention

The present invention will be further described in the following examples.

15

#### Comparative Example 1

A silica granule was prepared according to EP-A-670,712. A single silica of high structure, Sorbosil TC15 ( obtainable from Joseph Crosfield and Sons - England ) was agglomerated at 200 g powder batch size, laboratory scale with deionised water (water:solids ratio of 2.1:1) using a Sirman SV6 mixer, supplied by Metcalfe Catering Equipment Ltd, Blaenau Ffestiniog, Wales.

20

25

The resulting wet agglomerate was then dried in an oven at 150°C for 4 hours, gently forced through a 500 micron screen and sieved at 106 microns to adjust the particle size distribution.

30

The silica has the following properties:

Sorbosil TC15\*

Oil Absorption (cm <sup>3</sup> /100g)	339
Weight mean particle size: D10	5.6
(microns) D50	12.9
D90	29.3
Surface Area (m <sup>2</sup> g <sup>-1</sup> )	260

\* - Obtainable from Crosfield Ltd, England.

In order to determine the granule composition strength and breakdown characterisation, the agglomerated silica granule was subjected to ultrasonification using a Microson XL2020 Sonicator as described in part iii) of tests and definitions.

The weight of granule used in the test was 1g and deionised water was added to achieve a final weight of 200 g. The ultrasonic processor was programmed for timed and pulsed mode to achieve maximum amplitude at the tip for a period of 7 minutes. The processor was programmed to pulse on for 30 seconds and pulse off for 20 seconds to achieve a total process time of 7 minutes with minimum heat increase. The output control knob was turned to setting 10 to achieve a maximum amplitude of 60 microns at the tip and the programme started. The temperature of the dispersion was continuously monitored and was found to rise to 42°C.

When cavitation was complete the inorganic particle dispersion was poured through a 45 micron sieve and dried to constant weight as described in part iii) of tests and definitions.

In order to determine the wet sieve residue retained at 45 microns with no ultrasonification the same weight of agglomerate:water was used as described above. The inorganic particle dispersion was stirred to maintain dispersion with a spatula and poured straight through a 45 micron sieve, washed through with 100 cm<sup>3</sup> of de-ionised water and dried to constant weight as described in part iii) of tests and definitions.

#### Comparative Example 2

Two silicas one of high structure, Sorbosil TC15 and medium, bordering upon low structure, Sorbosil AC77 (obtainable from Crosfield Ltd, England.) were blended together in 1:1 ratio by weight and agglomerated at 200 g powder batch size, laboratory scale with de-ionised water (water: solids ratio of 1.33:1) using a Sirman SV6 mixer, supplied by Metcalfe Catering Equipment Ltd, Blaenau Ffestiniog, Wales.

The resulting wet agglomerate was then dried in an oven at 150°C for 4 hours, gently forced through a 500 micron screen and sieved at 106 microns to adjust the particle size distribution.

Sorbosil AC77 has the following properties:

Sorbosil AC77\*

Oil Absorption (cm <sup>3</sup> /100g)	129
Weight mean particle size: D10 (microns)	2.7
D50	8.1
D90	17.8
Surface Area (m <sup>2</sup> g <sup>-1</sup> )	120

The granule composition strength and breakdown characterisation of the agglomerated silica was carried out as described in Example 1.

Example 3 of the Invention

Two silicas, one of medium bordering upon low structure, Sorbosil AC39\* and medium structure Neosyl AC\* were blended together in a 3:1 ratio by weight. The resulting silica blend was agglomerated at 200 g powder batch size, laboratory scale with deionised water (water: solids ratio of 1.1:1) using a Sirman SV6 mixer, supplied by Metcalfe Catering Equipment Ltd, Blaenau Ffestiniog, Wales.

\* - Obtainable from Crosfield Ltd, England.

The resulting wet agglomerate was then dried in an oven at 150°C for 4 hours, gently forced through a 500 micron screen and sieved at 106 microns to adjust the particle size distribution.

The silicas have the following properties:

PROPERTY	Sorbosil AC39(*)	Neosyl AC(*)
OIL ABSORPTION (g/100g)	125	155
WEIGHT MEAN D <sub>10</sub>	3.2	3.7
PARTICLE SIZE D <sub>50</sub>	11.3	11.9
(microns) D <sub>90</sub>	31.7	38.1

\* - Obtainable from Crosfield Ltd, England.

The granule composition strength and breakdown characterisation of the agglomerated silica was carried out as described in Example 1.

Example 4 of the Invention

Two silicas, one of medium structure, Neosyl AC\* and medium,  
bordering upon low structure, Sorbosil AC35\* were blended  
together in a 9:1 ratio by weight. The resulting silica  
blend was agglomerated at 200 g powder batch size, laboratory  
scale with deionised water (water: solids ratio of 1.25:1)  
using a Sirman SV6 mixer, supplied by Metcalfe Catering  
Equipment Ltd, Blaenau Ffestiniog, Wales.

\* - Obtainable from Crosfield Ltd, England.

The resulting wet agglomerate was then dried in an oven at  
150°C for 4 hours, gently forced through a 500 micron screen  
and sieved at 106 microns to adjust the particle size  
distribution.

ISorbosil AC35 has the following properties:

Sorbosil AC35\*

Oil Absorption (cm <sup>3</sup> /100g)	100
Weight mean particle size: D10 (microns)	1.6
D50	10.0
D90	29.7

Example 5 of the Invention

Two silicas, one of medium bordering upon low structure,  
Sorbosil AC39\* and medium structure Neosyl AC\* were blended  
together in a 9:1 ratio by weight. The resulting silica  
blend was agglomerated at 200g powder batch size, laboratory  
scale with deionised water ( water: solids ratio of 1.1:1 )  
using a Sirman SV6 mixer, supplied by Metcalfe Catering  
Equipment Ltd, Blaenau Ffestiniog, Wales.

\* - Obtainable from Joseph Crosfield & Sons, England.

The resulting wet agglomerate was then dried in an oven at 150 °C for 4 hours, gently forced through a 500 micron screen and sieved at 106 microns to adjust the particle size distribution.

Example 6 of the invention

A coloured agglomerate was prepared with the same silica composition blend as example 3, to 97% with 3% Ultramarine Blue Grade 54\* incorporated in the silica blend. The same processing, drying and particle size adjustments were followed as described in example 3.

\* Supplied by Holliday Pigments, Humberside, England

Results:

Below are the results of the % agglomerate residue retained on the 45 micron sieve.

Agglomerate I.D.	No Ultra- sonification	60 microns of amplitude for 7 mins.
EX 1	95	57
EX 2	91	40
EX 3	79	0
EX 4	88	1
EX 5	90	0
EX 6	95	0

It can be seen that prior art silica granule made according to WO 94/12151 is too strong and does not breakdown to particles which cannot be felt on the skin. Similarly, a weaker granule in which half of the high structured Sorbosil TC15 silica is replaced with a much lower structured silica, Sorbosil AC77, is still much too strong for this type of application, where an optimum product such as examples 3 to 6 fully break down and can no longer be felt on the skin.

Example 7 (Facial Scrub)

The following oil-in-water ( O/W ) emulsion was prepared in which inorganic materials according to examples 1 to 4 were used.

<u>Component</u>	<u>%wt</u>
<u>Phase A</u>	
Inorganic material	5.00
Mineral oil	20.00
Primary alcohols, mixture <sup>1</sup>	10.00
Glyceryl Stearate SE	4.00
Ceteareth-12	1.50
Ceteareth-20	1.50
Glyceryl monooleate	1.00
Propylparaben	0.05
<u>Phase B</u>	
Deionised water	to 100%
Methylparaben	0.10
<u>Phase C</u>	
Fragrance	qs

<sup>1</sup>Acropol 35 ( ex Exxon Chemicals France )

Procedure

1. Add the ingredients of Phase A in the order shown and stir at 1000rpm. Heat to 70 °C.
2. Heat Phase B to 75 °C. When at temperature add Phase B to Phase A with stirring maintained at 1000rpm. When homogenous cool to 40 °C.
3. Add Phase C and mix thoroughly at low stirrer speed.

When used by trained panellists, it was found that Examples 1 and 2 lead to harsh initial skin feeling and particles left a gritty residue after 2 minutes rubbing on the skin ( by rubbing between the palms of the hands ). No lathery effect was perceived. This technique of rubbing between the palms of the hands was used in subsequent examples 8 to 10 to evaluate agglomerate breakdown on the skin.

Example 4 lead to a good initial skin feel where the particles were perceived and broke down in 25 seconds. A creamy smooth lather resulted.

Example 3 lead to good initial skin feel where the particles were perceived and broke down in 17 seconds. A creamy smooth lather resulted leaving a fresh clean feel.

Example 8 ( Shower gel )

The following shower gel composition was produced using the agglomerate according to example 3 as the inorganic material.

<u>Component</u>	<u>%wt</u>
Sodium lauryl ether sulphate <sup>2</sup> ( 27% )	12.00
Cocamidopropyl betaine <sup>3</sup> ( 30% )	2.00
Coconut Diethanolamide <sup>4</sup>	1.00
Inorganic material	5.00

Sodium chloride	10.00
Perfume, colouring, preservatives	qs
Deionised water	to 100%

- 5     <sup>2</sup> Empicol ESB3/M ( ex. Albright & Wilson )  
       <sup>3</sup> Empigen BS/P     ( ex. Albright & Wilson )  
       <sup>4</sup> Empilan CDE        ( ex. Albright & Wilson )

Procedure:

- 10     1. Dissolve salt or other lamellar phase-forming component in  
          water, without heating.  
          2. Add preservative  
          3. Add particulate material with mixing.  
          4. Add sodium lauryl ether sulphate.  
 15     5. Add any other optional ingredients, eg opacifier,  
          pearlescer, colourant, perfume, etc.  
          6. Finally add cocamidopropyl betaine and coconut  
          diethanolamide.
- 20     The shower gel with agglomerate according to example 3 lead  
          to good initial skin feel where the particles were perceived  
          and broke down in 17 seconds. A creamy smooth lather resulted  
          leaving a fresh clean feel.

25     Example 9 ( Shower gel )

The following shower gel composition was produced using the  
 agglomerate according to example 5 as the inorganic material.

30	<u>Component</u>	<u>%wt</u>
	Sodium lauryl ether sulphate <sup>2</sup> ( 70% )	12.00
	Cocamidopropyl betaine <sup>3</sup> ( 30% )	2.00
	Coconut Diethanolamide <sup>4</sup>	1.00
	Inorganic material	5.00
35	Amorphous silica <sup>5</sup>	3.00

Sodium chloride	5.00
Perfume, colouring, preservatives	qs
Deionised water	to 100%

<sup>2</sup> Elfan NS 243S ( ex. Akzo )

<sup>3</sup> Empigen BS/P ( ex. Albright & Wilson )

<sup>4</sup> Empilan CDE ( ex. Albright & Wilson )

<sup>5</sup> Amorphous silica thickener according to patent no WO 94/11302 with the particle size distribution adjusted to D<sub>10</sub> 1.1um, D<sub>50</sub> 4.4um and D<sub>90</sub> 9.2um obtainable from Joseph Crosfield & Sons, England.

Procedure:

1. Dissolve salt or other lamellar phase-forming component in water and heat to ~70°C.

2. Disperse silica thickener thoroughly.

3. Add preservative

4. Add particulate material with mixing.

5. Add sodium lauryl ether sulphate.

6. Cool to ~50°C and add any other optional ingredients, eg opacifier, pearlescer, colourant, perfume, etc.

7. Finally add cocamidopropyl betaine and coconut diethanolamide and cool to room temperature

The shower gel with agglomerate according to example 5 lead to good initial skin feel where the particles were perceived and broke down in 12 seconds. A creamy smooth lather resulted leaving a fresh clean feel.

Example 10 ( Clear facial gel )

The following facial gel composition was produced using the agglomerate according to example 6 as the inorganic material.

<u>Component</u>	<u>%wt</u>
Ammonium lauryl sulphate <sup>6</sup> ( 30% )	50.00
Cocamidopropylbetaine ( 30% )	15.00
Carbomer <sup>7</sup>	1.55
5 Inorganic material ( as per example 6 )	1.00
Perfume, preservatives	qs
Water	to 100%

<sup>6</sup> Empicol AL30/T ( ex. Albright & Wilson )

10 <sup>7</sup> Carbopol Ultrez 10 ( ex. B.F. Goodrich )

Procedure:

1. Disperse carbomer thoroughly in water and increase temperature to ~50°C and mix for 20 mins.
  - 15 2. Switch off heat and add preservatives and perfume.
  3. Add surfactants and mix thoroughly.
  4. Finally cool to room temperature and stir in inorganic material.
- 20 The clear facial gel with agglomerate according to example 6 lead to good initial skin feel where the coloured visible particles in a clear base were perceived and broke down in 20 seconds. A creamy smooth lather resulted leaving a fresh clean feel.

**CLAIMS**

1. Inorganic material in granular form having a granular strength such that less than 5%, preferably less than 2%, most preferably less than 1% by weight, residue remains on a 45 micron wet sieve after ultrasonification for 7 minutes with 60 micron amplitude of vibration.
2. Inorganic material according to claim 1 comprising at least 95% by weight of amorphous silicas.
3. Inorganic material according to claim 2 comprising at least 95% by weight of amorphous silica agglomerates.
4. Inorganic material in granular form according to claim 1, 2 or 3 comprising at least 95% w/w of a water insoluble particulate, whereby 5 to 90% of the water insoluble particulate is made from a water insoluble particulate material, having a weight mean particle size of less than 20 microns and an oil absorption capacity of 90 to 145 cm<sup>3</sup>/100g, and selected from the group consisting of amorphous silicas, aluminas, calcium carbonates, dicalcium phosphate, tribasic calcium phosphates, insoluble sodium metaphosphate, calcium pyrophosphates, hydroxyapatites, perlites, zeolites, magnesium carbonate, pumice, and 5 to 90% of the water insoluble particulate is made from an amorphous silica, having a weight mean particle size of below 20 microns and an oil absorption 150 to 190 cm<sup>3</sup>/100g.
5. Inorganic material in granular form according to claim 1, 2 or 3 comprising at least 95% w/w of a water insoluble particulate, whereby 5 to 90% of the water insoluble particulate is made from a water insoluble particulate material, having a weight mean particle size

of less than 20 microns and an oil absorption capacity of 90 to 145 cm<sup>3</sup>/100g, and selected from the group consisting of aluminas, calcium carbonates, dicalcium phosphate, tribasic calcium phosphates, insoluble sodium metaphosphate, calcium pyrophosphates, hydroxyapatites, perlites, zeolites, magnesium carbonate, pumice, and 5 to 90% of the water insoluble particulate is made from an amorphous silica, having a weight mean particle size of below 20 microns and an oil absorption 130 to 190 cm<sup>3</sup>/100g.

6. Inorganic material in granular form according to claim 4 having a particle size of 95% below 1000 microns and 95% above 45 microns, as measured by sieve analysis.

7. Inorganic material in granular form according to claim 5 having a particle size of 95% below 1000 microns and 95% above 45 microns, as measured by sieve analysis.

8. Cosmetic composition comprising 1 to 20% by weight, preferably 1 to 10% by weight, of an inorganic material according to claims 1 to 7.

9. Cosmetic composition including an inorganic material in granular form, characterised in that the inorganic material in granular form, under condition of use of the cosmetic composition, breaks down to a particle size wherein less than 5% by weight, preferably less than 2% by weight, most preferably less than 1% by weight is above 45 microns, as measured by wet sieve analysis.

# INTERNATIONAL SEARCH REPORT

International Application No <b>PCT/EP 97/00202</b>		
<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 6 C09C1/30 A61K7/00 C09C1/00 C09C3/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 6 C09C A61K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 15, no. 293 (C-853), 25 July 1991 & JP 03 106984 A (MITSUBISHI KASEI CORP.), 7 May 1991, see abstract	1
P,A	--- WO 96 30304 A (RHONE-POULENC CHIMIE) 3 October 1996 see page 3, line 10-28; claim 21	1
P,A	--- DE 195 31 044 A (NIPPON OIL CO.) 29 February 1996 see claim 1	1
A	--- FR 2 303 763 A (RHONE-POULENC INDUSTRIES) 8 October 1976 --- <div style="text-align: center;">-/--</div>	
<div style="display: flex; justify-content: space-between;"> <span><input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.</span> <span><input checked="" type="checkbox"/> Patent family members are listed in annex.</span> </div>		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search	Date of mailing of the international search report	
7 April 1997	14.04.97	
Name and mailing address of the ISA	Authorized officer	
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van Bellingen, I	

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 97/00202

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 94 12151 A (UNILEVER) 9 June 1994 cited in the application -----</p>	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/EP 97/00202

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9630304 A	03-10-96	FR 2732328 A AU 5338196 A CA 2191486 A EP 0762993 A	04-10-96 16-10-96 03-10-96 19-03-97
DE 19531044 A	29-02-96	JP 8059727 A CA 2156690 A	05-03-96 24-02-96
FR 2303763 A	08-10-76	AU 505536 B AU 1143676 A BE 839462 A BR 7601454 A CA 1093789 A CH 612897 A DE 2610207 A GB 1536199 A JP 1677474 C JP 51136841 A JP 62050403 B LU 74534 A NL 7602568 A SE 413237 B SE 7602791 A SE 446503 B SE 7907276 A US 4336245 A US 4422880 A US 4132806 A US 4157920 A US 4161455 A	22-11-79 01-09-77 13-09-76 14-09-76 20-01-81 31-08-79 23-09-76 20-12-78 13-07-92 26-11-76 24-10-87 11-07-77 14-09-76 12-05-80 13-09-76 22-09-86 31-08-79 22-06-82 27-12-83 02-01-79 12-06-79 17-07-79
WO 9412151 A	09-06-94	AU 5626094 A DE 69304340 D DE 69304340 T EP 0670712 A ES 2092395 T JP 8503480 T ZA 9308753 A	22-06-94 02-10-96 06-02-97 13-09-95 16-11-96 16-04-96 23-05-95